Gas Chromatography-Mass Spectrometry-Mass Spectrometry

Gas chromatography-mass spectrometry-mass spectrometry (GC-MS-MS) is used to analyze complex mixtures of volatile and semi-volatile organic—and occasionally inorganic—compounds. The MS-MS instrument has other sample introduction methods besides GC. A pyrolysis probe can be used to introduce off-gases produced by heating solids into the MS-MS. Thermal desorption of analytes from a charcoal trap and direct introduction of a solid sample into the MS-MS is also possible. MS-MS can be used to elucidate molecular structures and to study ion–molecule reactions.

Principles of Technique

A GC-MS-MS instrument can be operated as a normal single-stage mass spectrometer (see GC-MS). Both electron–impact and chemical ionization techniques are available, and both positive and negative ions can be detected.

Tandem mass spectrometry (MS-MS) allows an extra stage of separation following a collision or reaction. As in single-stage MS, a sample is introduced into a source and ionized. The resulting ions are extracted from the source and passed into the first mass filter, which, in this example, is a quadrupole mass filter. Only ions of a selected mass-to-charge ratio are passed into the second quadropole, a collision region pressurized at ~1 mTorr. This quadrupole is operated in an "rf only" mode, which has minimum filtering and strong refocusing properties for the ions. Ions collide with the collision gas (usually argon for collisionally activated dissociation) and fragment to form product ions. These products are passed into the scanning third quadrupole and the resulting ions detected with a channeltron electron multiplier. Passing a single parent ion into an inert collision gas and scanning the third quadrupole generates the mass spectrum of the daughter ion.

Tandem MS also enables the study of ion–molecule reactions. If the collision cell is pressurized with a reactive gas, ions can be selected using the first quadrupole for a specific collision. These collisionally activated reaction products are then analyzed with the third quadrupole. LLNL has both triple quadrupole and ion-trap mass spectrometers.

Thermal MS uses a third-generation, pyrolysis furnace designed at LLNL. Samples are heated at a known rate (between 1°–30°C/min) to a maximum of 1000°C in an argon flow (20–250 mL/min). The argon containing pyrolysis products is then analyzed by the mass spectrometer. In addition, a pyrolysis solids insertion probe capable of ballistically heating a sample to 1000°C for direct pyrolysis MS is available.

A gas inlet enables the analysis of standards, bottled samples, and pyrolysis furnace gases under identical conditions. This completely heated inlet system also provides the

Examples of Applications

GC-MS

- Analysis of petroleum oil and shale oil.
- Pollutants in air, water, and solid waste.
- Drugs and their metabolites.
- Explosives.
- Pesticides.
- Additives, such as antioxidants and plasticizers in plastics or aerogels.

Pyrolysis MS

- Direct analysis of off-gases from the pyrolysis of oil shale, coal, plastics, polymers, and aerogels.

Thermal Desorption MS

- Analysis of volatile organics trapped on sampling tubes (charcoal, Tenax) for air quality analysis, pollution monitoring, and explosives residue.

Direct Insertion Probe MS

- Determination of unknown solids and confirmation of synthesized organic and inorganic compounds, including polymers and aerogels.

MS-MS

- Identification of unknowns in mixtures.
- Extremely selective detection of target compounds in complex matrices (e.g., sulfur gases from the pyrolysis of oil shale).
- Ion–molecule reactions (e.g., determinations of CO at *m/z* 28 in the presence of hydrocarbons, also at *m/z* 28).

capability to standardize and perform water determinations in unknown gas samples.

A thermal desorption and cryofocusing unit is attached to the gas chromatograph. Samples absorbed onto charcoal or Tenax are thermally desorbed in a helium carrier gas and cryogenically trapped. The trap is then quickly heated, releasing the sample to the GC-MS-MS where it is analyzed.

Samples

Form. Solids, liquids, and gases; most organics and some inorganics.

Size. GC-MS requires an injection of 0.2 to 5 µL containing 1 to 200 ng for a routine analysis of each compound, and possibly as little as 10 pg in specific cases.

Pyrolysis MS requires 0.1 to 2 g of ground solid. Gas MS needs a minimum of 1 L at 1 atm. Thermal desorption MS samples are absorbed on either a 1/4- or 5/8-in. sample tube; other sample types are available upon request. Direct insertion probe MS requires 1 to 100 mg of either a solid or liquid sample.

Tandem MS-MS can be performed with any of the techniques listed here with the same sample size requirements.

Preparation. Samples must conform to the size restrictions given above. Contact the analyst for more information regarding the preparation of samples.

Limitations

Compounds must be ionizable in the mass spectrometer. The detection limit can be as low as 10 pg, depending on the technique and the sample.

Estimated Analysis Time

Analysis of a sample for one compound requires a minimum of 30 min. A typical GC-MS analysis for unknowns requires 45 min to 3 h of instrument time, and from 15 min to several days to analyze the results. Additional time may be required for preparation of standards for quantitative analysis.

Capabilities of Related Techniques

The present GC-MS-MS instrument can be operated as a simple GC-MS, but the extra power of tandem mass spectrometry often adds greater selectivity and sensitivity (see GC-MS for other related organic analysis techniques).

Gas mass spectrometry is preferred for the analysis of mixtures of gases and when high quantitative accuracy is required, but it cannot directly determine analytes in water.

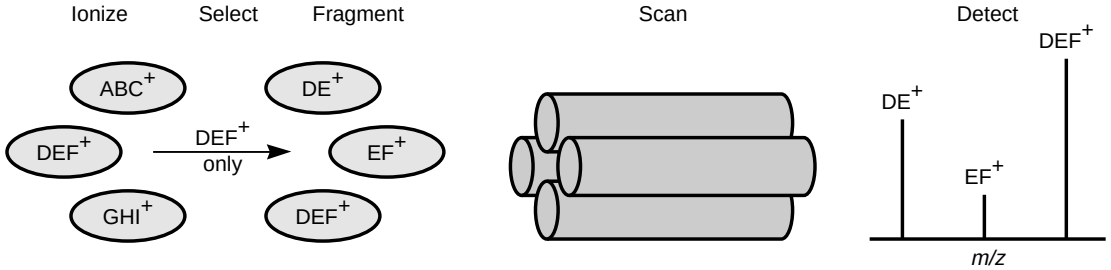

Illustration of the principle of MS-MS. A molecule is ionized in the MS source. One specific ion (DEF^+) is allowed to pass through the first quadrupole into a collision cell. This ion is fragmented; the spectrum of the resulting ions is scanned using the third quadrupole and then detected by an electron multiplier.

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